N legs 10. (Electrons flow in the opposite direction.) These patents disclose superlattice layers comprised of: (1) SiGe as conducting layer and Si as a barrier layer and (2) alternating layers of two different alloys of boron carbide. In the '387 patent Applicants disclose that they had discovered that strain in the layers can have very beneficial effects on thermoelectric properties of the elements disclosed in the '467 patent.

A1 end

In the Claims:
Please amend Claim 1 and 2 as follows:

A2

1. (Amended) A thermoelectric module comprised of:
   A) a plurality of n-legs comprised of at least 100 very thin alternating layers of silicon and silicon carbide; and
   B) a plurality of p-legs;

   said p-legs and said n-legs being electrically connected to produce said thermoelectric module.

2. (Amended) A thermoelectric module as in Claim 1 wherein said p-legs comprise at least 100 very thin alternating layers of boron carbide.

## REMARKS

### Drawings

The drawings have been corrected as suggested by the Examiner and the specification has been amended to refer to numbers in the drawings as suggested by the Examiner.

### Claims

The claims have been narrowed to require at least 100 alternating layers of Si/SiC in the n-legs of the thermoelectric modules.

### Section 103 Rejection – Golecki

Examiner rejected all claims as being unpatentable over Golecki combined with Applicants' admitted prior art or with the above references and the teachings of Ghamaty. Applicants request reconsideration.

There is no suggestion in any of the individual references for the combinations proposed by Examiner. Only a very few thin film materials provide thermoelectric properties. Applicant has shown as a result of many years of research and development that an excellent thermoelectric module can be made with of n-legs comprised of a large number of very thin alternating layers of Si and SiC combined with p-legs. As stated in the

summary of the application, Applicants expected that their preferred embodiment could provide module efficiencies of about 30 percent! This is an amazing efficiency given that state of the art thermoelectric modules have efficiencies in the range of about 5 percent. Applicants expect this module to revolutionize the thermoelectric industry!

Applicants' projection of about 30 percent efficiency has been supported by subsequent developments by applicants as shown by the attached news release dated August 25, 2002 in which Applicants' employer discloses actual test data showing a 14 percent efficiency of an early prototype unit.

The Golecki patent for placing a thin film of SiC on a silicon substrate was published in 1993. Superlattice quantum well thermoelectric materials have been proposed since 1983 (see background section of the present application). Had the combination of the Golecki teaching and the known advantages of certain specific superlattices for making thermoelectric materials been obvious then someone would have tried it long before Applicants demonstrated their breakthrough invention.

There is nothing in the prior art that suggests this combination. Examiner is correct that the admitted prior art teaches that quantum well thermoelectric modules can be made with very thin films. Examiner is also correct that Golecki teaches a method of depositing a thin film of SiC on to a silicon substrate. Golecki <u>claims</u> alternating layers of silicon and silicon carbide but there is no suggestion in his specification that he <u>actually produced</u> such layers. And there is certainly no suggestion that his process could be used to produce at least 100 alternating layers, nor is there any suggestion in Golecki that his process could be used to make thermoelectric modules or that thin layers of Si/SiC could be used to make thermoelectric modules. Also, there is no suggestion in any of the other references cited by Examiner that the thin layers of Si/SiC could be used to make thermoelectric modules as claimed by Applicants. Applicants have amended their claims to limit them to at least 100 layers of Si/SiC which is the number of layers in Applicants' proof of principal demonstration discussed on page 6 of the application.

## Golecki Teaches Away from the Present Invention

Not only is there nothing in Golecki to suggest that his thin film of SiC could be used to make thermoelectric elements, his patent actually teaches away from such use. At Col 9, line 37 Golecki reports that the SiC films have <u>high</u> electrical resistivity. This is exactly opposite of what is needed for good thermoelectric materials. See the explanation in Ghamaty (US Patent 6,096,965) at Col. 1 lines 13-26. Ghamaty explains: "Therefore, in searching for a good thermoelectric material, we look for large values of S (Seebeck coefficient) and <u>low values of $\rho$</u> (electrical resistivity).

## Conclusion

There is nothing in the prior art to suggest the combinations proposed by Examiner. There is no evidence that Golecki ever made a multi-layer product of silicon and silicon carbide and there is certainly no evidence that if one were made by the Golecki process, that it could be used to make a practical thermoelectric module as claimed by Applicants.

In fact, Golecki actually teaches away from such use by pointing out that his SiC layer has high electrical resistivity!

Therefore for all of the above reasons, Applicants submit that the claims as amended are not disclosed or suggested by the referenced prior art and that the claims should be allowable and Applicants request that they be allowed and that the application be allowed to issue as a patent.

Respectfully submitted,

John R. Ross
Regis. No. 30,530
PO Box 2138
Del Mar, CA 92014
858-755-3122

MARKED UP COPY SHOWING CHANGES

# THERMOELECTRIC DEVICE WITH Si/SiC SUPERLATTICE N-LEGS

The present invention relates to thermoelectric devices and in particular to very thin lattice thermoelectric devices.

## BACKGROUND OF THE INVENTION

Workers in the thermoelectric industry have been attempting too improve performance of thermoelectric devices for the past 20-30 years with not much success. Most of the effort has been directed to reducing the lattice thermal conductivity (K) without adversely affecting the electrical conductivity. Experiments with superlattice quantum well materials have been underway for several years. These materials were discussed in an paper by Gottfried H. Dohler which was published in the November 1983 issue of Scientific American. This article presents an excellent discussion of the theory of enhanced electric conduction in superlattices. These superlattices contain alternating conducting and barrier layers and create quantum wells that improve electrical conductivity. These superlattice quantum well materials are crystals grown by depositing semiconductors in layers whose thicknesses is in the range of a few to up to about 100 angstroms. Thus, each layer is only a few atoms thick. (These quantum well materials are also discussed in articles by Hicks, et al and Harman published in Proceedings of 1992 1st National Thermoelectric Cooler Conference Center for Night Vision & Electro Optics, U.S.Army, Fort Belvoir, Virginia. The articles project theoretically very high ZT values as the layers are made progressively thinner.) The idea being that these materials might provide very great increases in electric conductivity without adversely affecting Seebeck coefficient or the thermal conductivity. Harmon of Lincoln Labs, operated by MIT has claimed to have produced a superlattice of layers of (Bi,Sb) and Pb(Te,Se). He claims that his preliminary measurements suggest ZTs of 3 to 4. FIG. 1 shows theoretical calculated values (Sun et al – 1998) of ZT plotted as a function of quantum well width.

The present inventors have actually demonstrated that high ZT values can definitely be achieved with $Si/Si_{0.8}Ge_{0.2}$ superlattice quantum well (See, for example, US Patent No.

5,550,387.) Most of the efforts to date with superlattices have involved alloys that are known to be good thermoelectric materials for cooling, many of which are difficult to manufacture as superlattices. The present inventors have had issued to them United States patents in 1995 and 1996 which disclose such materials and explain how to make them. These patents (which are hereby incorporated by reference herein) are US Patent Nos.: 5,436,467, 5,550,387. FIGS. 1A and 1B herein were FIGS. 3 and 5 of the "467 patent. A large number of very thin layers (in the '467 patent, about 250,000 layers) together produce a thermoelectric leg 10 about 0.254 cm thick. In the embodiment shown in the figures all the legs are connected electrically in series with a sprayed-on metal layer 14 and otherwise are insulated from each other in an egg-crate type thermoelectric element as shown in FIG. 1A. As shown by arrows 30 in FIG. 1B current flows from the cold side to the hot side through P legs 12 and from the hot side to the cold side through N legs 10. (Electrons flow in the opposite direction.) These patents disclose superlattice layers comprised of: (1) SiGe as conducting layer and Si as a barrier layer and (2) alternating layers of two different alloys of boron carbide. In the '387 patent Applicants disclose that they had discovered that strain in the layers can have very beneficial effects on thermoelectric properties of the elements disclosed in the '467 patent.

What are needed are better quantum well materials, even better than the ones discussed above, for thermoelectric devices.

## SUMMARY OF THE INVENTION

The present invention provides a superlattice thermoelectric device. The device is comprised of p-legs and n-legs, each leg being comprised of a large number of at least two different very thin alternating layers of elements. The n-legs in the device are comprised of alternating layers of silicon and silicon carbide. In preferred embodiments p-legs are comprised of a superlattice of B-C layers, with alternating layers of different stoichiometric forms of B-C. This preferred embodiment is designed to produce 20 Watts with a temperature difference of 300 degrees C with a module efficiency of about 30 percent. The module is about 1 cm thick with a cross section area of about 7 $cm^2$ and has

We Claim:

1. A thermoelectric module comprised of: at least 100

   A) a plurality of n-legs comprised of very thin alternating layers of silicon and silicon carbide; and

   B) a plurality of p-legs,;

   said p-legs and said n-legs being electrically connected to produce said thermoelectric module.

2. A thermoelectric module as in Claim 1 wherein said p-legs comprise at least 100 very thin alternating layers of boron carbide.

3. A thermoelectric module as in Claim 2 wherein said very thin alternating layers of boron carbide comprise two different stoichiometric forms of boron carbide.

4. A thermoelectric module as in Claim 3 wherein said very thin alternating layers of boron carbide are alternating layers of $B_4C$ and $B_9C$.

5. A thermoelectric module as in Claim 2, wherein said plurality of n-legs is comprised of a plurality of very thin alternating layers of silicon and silicon-carbide and said very thin alternating layers of boron carbide are alternating layers of $B_4C$ and $B_9C$.

6. A thermoelectric module as in Claim 1 wherein said alternating layers are deposited on a substrate.

7. A thermoelectric module as in Claim 6 wherein said substrate is silicon.

8. A thermoelectric module as in Claim 6 wherein said substrate is silicon film.

9. A thermoelectric module as in Claim 6 wherein said substrate is a polyimide substrate.

10. A thermoelectric element as in Claim 9, wherein said polyimide substrate is Kapton®.

11. A thermoelectric element as in Claim 10, wherein said polyimide substrate is Kapton® film.

12. A thermoelectric element as in Claim 1, wherein said very thin alternating layers are each less than 100nm thick.

13. A thermoelectric element as in Claim 1 wherein said very thin alternating layers are each about 10 nm thick.

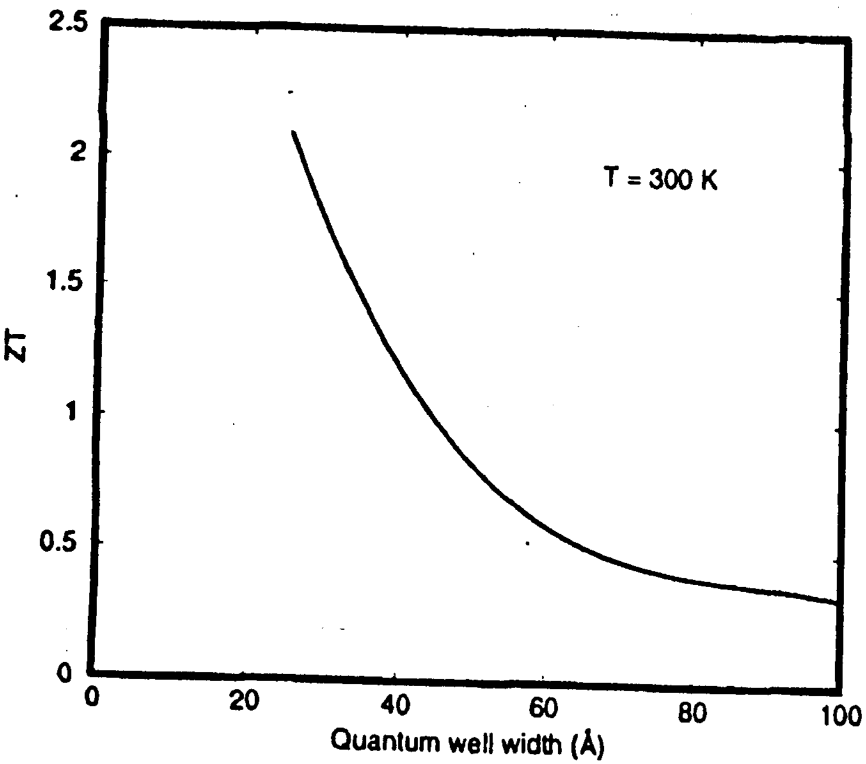



FIG. 1

PRIOR ART

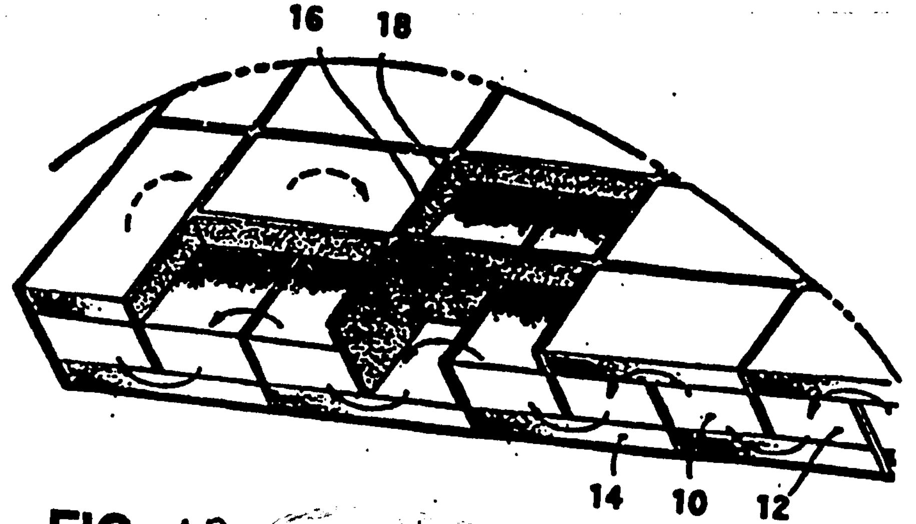
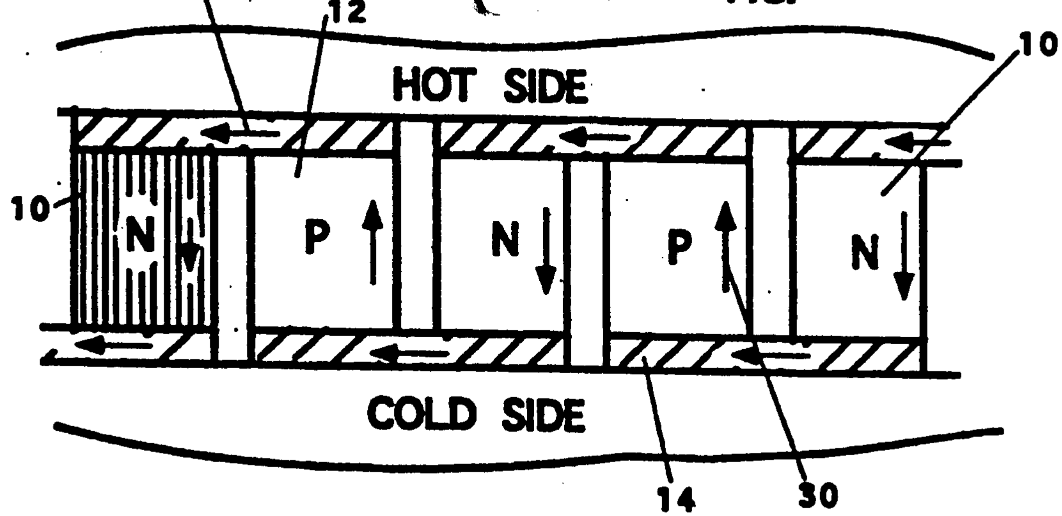



FIG. 1A PRIOR ART

PRIOR ART

FIG. 1B




Approved by Examiner
MAO 3-12-03

August 25, 2002

# NEWS RELEASE
## Hi-Z Announces High Efficiency Thermoelectric Materials

Hi-Z Technology, Inc., based in San Diego, is developing new Quantum Well (QW) thermoelectric materials that have recently exhibited 14% efficiency and are expected to yield conversion efficiencies several times that of present day materials. QWs are nanostructured multilayer films. Based on recent experimental work, Hi-Z anticipates thermal to electric conversion efficiencies of 25-40% at a $T_H$ of 250°C to 700°C and a $T_C$ of 50°C to 100°C. These QW materials are in development for recovering waste heat from trucks and automobiles engines, but they may also be used in any direct conversion of heat to electricity such as for auxiliary power units, self powered appliances and space power supplies.

The breakthrough that makes thermoelectrics an attractive choice for energy conversion is the large increase in efficiency made possible by the use of quantum well (QW) materials. With funding from the DOE and DOD, Hi-Z has recently measured power and efficiency demonstrating a QW couple conversion efficiency of 14% on a couple that combined a multilayer QW of P type $B_4C/B_9C$ with a QW of N type Si/SiGe, Figure 1. This couple operated between 70°C and 250°C and was fabricated on a 5μm thick Si substrate with ~11μm thick QWs. The efficiency was calculated by dividing the electric power out of the couple by the electric power into the heater. The 14% efficiency was obtained with no correction for any extraneous heat losses, such as through the Si substrate and the heater wires. The experimental set up also confirmed a known efficiency of ~5.5% for presently used $Bi_2Te_3$ bulk alloys, assuring the experimental setup accuracy. The 14% data point and the predicted values agree quite well Figure 2. A ZT of ~4 at T=150•C was back calculated from this efficiency measurement. In another separate confirming experiment, at a lower temperature, the $B_4C/B_9C$ film was used as a cooler creating a maximum • T difference of ~45°C. This temperature difference yields a ZT~3 for T~25°C. The QW film was the same $B_4C/B_9C$ material used in the couple mentioned above for measuring the efficiency. The QW layers were deposited by sputtering. Each layer is 100 Angstrom thick for a total of ~11μm or 1100 layers.

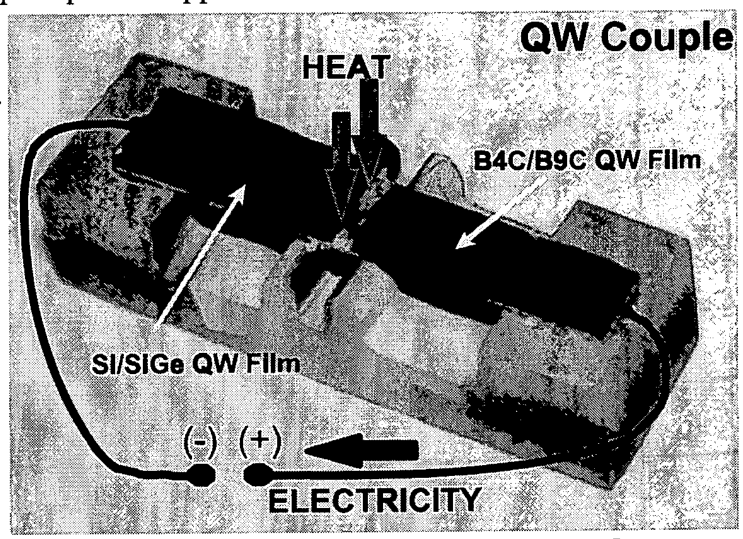


Figure 1. Quantum Well Thermoelectric Couple on 5μm Si

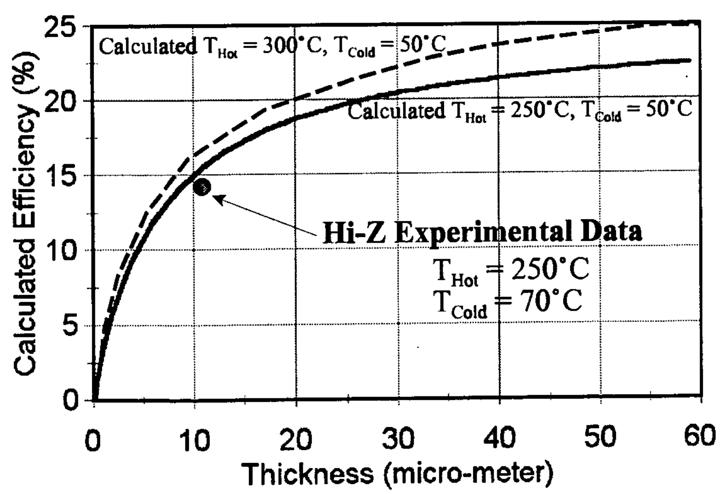


Figure 2. Effici ncy of QW coupl versus film thickness on a 5• m Si substrat . Hi-Z xperimental and predict d valu s ar shown f r c mparison for N type Si/SiGe and P type $B_4C/B_9C$.